学校编码：10384　　分类号_____密级 非公开

学号：20520091151431　　UDC_____

厦门大学

硕 士 学 位 论 文

小分子燃料电催化氧化反应的原位红外光谱研究

In situ FTIR Spectroscopic Studies of Electrocatalytic Oxidation of Small Fuel Molecules

林建龙

指导教师姓名：周 志 有 副教授

孙 世 刚 教 授

专 业 名 称：应用化学

论文提交日期：2012 年 6 月

论文答辩时间：2012 年 6 月

学位授予日期：2012 年 6 月

答辩委员会主席：_____

评 阅 人：_____

In situ FTIR Spectroscopic Studies of Electrocatalytic Oxidation of Small Fuel Molecules

A Dissertation Submitted to the Graduate School of Xiamen University for the Degree of

Master of Science

By

Jian-Long Lin

This work was carried out under the supervision of

Associate Prof. Zhi-You Zhou

Prof. Shi-Gang Sun

At

Department of Chemistry, Xiamen University

June 2012

厦门大学学位论文原创性声明

兹呈交的学位论文，是本人在导师指导下独立完成的研究成果。本人在论文写作中参考的其他个人或集体的研究成果，均在文中以明确方式标明。本人依法享有和承担由此论文而产生的权利和责任。

声明人（签名）：

年　　月　　日

厦门大学学位论文著作权使用声明

本人完全了解厦门大学有关保留、使用学位论文的规定。厦门大学有权保留并向国家主管部门或其指定机构送交论文的纸质版和电子版，有权将学位论文用于非赢利目的的少量复制并允许论文进入学校图书馆被查阅，有权将学位论文的内容编入有关数据库进行检索，有权将学位论文的标题和摘要汇编出版。保密的学位论文在解密后适用本规定。

本学位论文属于

1、保密（√），在 3 年解密后适用本授权书。

2、不保密（　）

（请在以上相应括号内打“√”）

作者签名：　　日期：　　年　月　日

导师签名：　　日期：　　年　月　日

目 录

中文摘要……I

英文摘要……II

第一章　绪论……1

§1.1 谱学电化学……1

§1.2 电化学原位红外反射光谱……2

§1.3 纳米结构表面的特殊红外性能……5

§1.3.1 表面增强红外光谱……5

§1.3.2 类 Fano 红外光谱……6

§1.3.3 异常红外效应……7

§1.4 增强红外吸收纳米材料的制备……8

§1.4.1 干法制备……8

§1.4.2 湿法制备……9

§1.5 燃料电池的工作原理……9

§1.6 燃料电池小分子电催化反应的研究进展……10

§1.6.1 乙醇电催化反应的研究进展……10

§1.6.2 乙二醇电催化反应的研究进展……12

§1.6.3 氨电催化反应的研究进展……14

§1.7 本论文的研究目的与设想……16

参考文献……17

第二章　实验与仪器……29

§2.1 试剂和溶液……29

§2.2 电化学体系……29

§2.2.1 本体 Pt、Pd 电极及枝晶状结构 Pt 电极的制备……29

§2.2.2 电化学装置……30

§2.2.3 电极表面 CO 饱和吸附……..……..30
§2.3 扫描电子显微镜 (SEM)……..……30
§2.4 电化学原位红外反射光谱实验……...30
§2.4.1 红外电解池……31
§2.4.2 红外光谱仪器……31
§2.4.3 原位红外反射光谱……..32
参考文献……34

第三章 乙二醇在本体 Pd 电极碱性介质中电氧化的原位红外光谱研究……36
§3.1 乙二醇在Pd上的电氧化……36
§3.1.1 乙二醇在Pd上电氧化的循环伏安特征……36
§3.1.2 乙二醇在Pd上电氧化的原位红外光谱研究……37
§3.1.3 定量分析乙二醇在Pd上氧化产物随电位的变化关系……41
§3.2 乙醇酸、乙二醛、乙醛酸在Pd上电氧化的原位红外光谱研究……43
§3.3 乙二醇及C2物种电氧化的相对选择性……46
§3.4 不同浓度乙二醇在Pd上电氧化……48
§3.4.1 不同浓度乙二醇在Pd上电氧化的循环伏安特征……48
§3.4.2 不同浓度乙二醇在Pd上电氧化的原位红外光谱研究……49
本章小结……54
参考文献……55

第四章 枝晶状 Pt 薄膜制备及其特殊红外效应……57
§4.1 枝晶状 Pt 薄膜的制备及表征……...57
§4.1.1 枝晶状Pt薄膜制备方法……57
§4.1.2 枝晶状Pt薄膜CV表征……...58
§4.1.3 枝晶状Pt薄膜SEM表征……60

§4.2 枝晶状Pt薄膜特殊红外性能研究……62
本章小结……67
参考文献……68

第五章　增强红外吸收枝晶 Pt 电极研究电催化反应过程……70
§5.1 Pt 黑、本体 Pt、枝晶 Pt 增强红外吸收比较……70
§5.1.1 Pt黑、本体Pt、枝晶Pt三种电极表面形貌SEM图比较……70
§5.1.2 Pt黑、本体Pt、枝晶Pt三种电极CV图比较……71
§5.1.3 Pt黑、本体Pt、枝晶Pt三种电极红外性能比较……72
§5.2 增强红外吸收枝晶Pt研究CO吸附……75
§5.3 增强红外吸收枝晶Pt研究乙醇电催化反应过程……76
§5.4 增强红外吸收枝晶Pt研究氨电催化反应过程……80
§5.4.1 NH_3在Pt上电氧化过程CV研究……80
§5.4.2 NH_3在Pt上电氧化过程原位红外光谱研究……81
本章小结……90
参考文献……91

结论……93

作者攻读硕士期间发表与交流的论文……95

致 谢……97

Table of contents

Abstract in Chinese……I

Abstract in English……II

Chapter 1 Introduction……1

§ 1.1 Spectroelectrochemistry……1

§ 1.2 Fourier transform infrared spectroscopy(FTIRS)……2

§ 1.3 Particular IR properties on nanostructure surfaces……5

§ 1.3.1 Surface enhanced IR Absorption(SEIRA)……5

§ 1.3.2 Fano-like infrared effects……6

§ 1.3.3 Abnormal IR effects……7

§ 1.4 The preparation of nanomaterials with IR enhanced absorption……8

§ 1.4.1 Dry preparation……8

§ 1.4.2 Wet preparation……9

§ 1.5 The principle of Fuel Cells……9

§ 1.6 Research on electrochemical reactions of small molecular of Fuel Cells..10

§ 1..6.1 Research progresses of electrooxidation of ethanol……10

§ 1..6.2 Research progresses of electrooxidation of ethylene glycol……12

§ 1..6.3 Research progresses of electrooxidation of ammonia……14

§ 1.7 Objectives and plans of the dissertation……16

References……17

Chapter 2 Experimental and instruments……29

§ 2.1 Reagents and solution……29

§ 2.2 Electrochemical system……29

§ 2.2.1 bulk Pt、Pd and the preparation of dendritic Pt thin films……29

§ 2.2.2 Electrochemical apparatus……30

§ 2.2.3 Formation of CO adlayer……30

§ 2.3 Scanning electron microscopy(SEM) ……..30

§ 2.4 Electrochemical in situ FTIR reflection spectroscopy……...31

§ 2.4.1 FTIRS electrochemical cells……31

§ 2.4.2 FTIR apparatus……31

§ 2.4.3 In situ FTIRS reflection spectroscopy……32

References……34

Chapter 3 In situ FTIR spectroscopic study of ethylene glycol electrooxidation on bulk Pd electrode in alkaline media……36

§ 3.1 Electrooxidation of EG on bulk Pd electrode……36

§ 3.1.1 CV studies of EG electrooxidation on bulk Pd electrode……36

§ 3.1.2 In situ FTIR spectroscopic studies of EG electrooxidation on bulk Pd electrode……..37

§ 3.1.3 Quantitative analysis of products of EG electrooxidation on bulk Pd electrode changing with potentials……..41

§ 3.2 In situ FTIR spectroscopic studies of glycolate、glyoxal and glyoxylate electrooxidation on bulk Pd electrode……...43

§ 3.3 The relative reaction selectivity of EG and its C2 species……46

§ 3.4 Electrooxidation of EG with different concentrations on bulk Pd electrode……...48

§ 3.4.1 CV studies of different EG concentrations electrooxidation on bulk Pd electrode……48

§ 3.4.2 In situ FTIR spectroscopic studies of different EG concentrations electrooxidation on bulk Pd electrode……49

Summary……54

References……...55

Chapter 4 Preparation of dendritic Pt thin films and their particular

infrared properties……..57

§ 4.1 Preparation and characterization of dendritic Pt thin films……..57

§ 4.1.1 Preparation of dendritic Pt thin films……57

§ 4.1.2 CV studies of dendritic Pt thin films…….58

§ 4.1.3 SEM studies of dendritic Pt thin films……..60

§ 4.2 In situ FTIR spectroscopic studies of CO adsorption on dendritic Pt thin films……..62

Summary……...67

References……68

Chapter 5 Application of dendritic Pt electrode with IR enhancement in studying electro-catalysis reaction……70

§ 5.1 Comparison of enhanced IR absorption of Pt black、bulk Pt and dendritic Pt……70

§ 5.1.1 SEM studies of Pt black、bulk Pt and dendritic Pt……..70

§ 5.1.2 CV studies of Pt black、bulk Pt and dendritic Pt…….....71

§ 5.1.3 In situ FTIR spectroscopic studies of CO adsorption on Pt black、bulk Pt and dendritic Pt……72

§ 5.2 Dendritic Pt electrode with IR enhancement studies the adsorption of CO…….....75

§ 5.3 Dendritic Pt electrode with IR enhancement studies the process of ethanol electrooxidation……...76

§ 5.4 Dendritic Pt electrode with IR enhancement studies the process of ammonia electrooxidation……80

§ 5.4.1 CV Studies of ammonia electrooxidation on Pt……....80

§ 5.4.2 In situ FTIR spectroscopic studies of ammonia electrooxidation on Pt…81

Summary……...90

References……91

Conclusions……...93

Publications list during M.S. study……..95

Acknowledgements……97

摘 要

本论文运用电化学循环伏安、原位红外反射光谱等技术研究了碱性介质中乙二醇（EG）在 Pd 电极上的电氧化过程，着重探索乙二醇氧化的 C2 物种和不同浓度乙二醇的电氧化机理并对反应产物进行定量分析。另外采用方波电位法在本体 Pt 上电沉积枝晶状 Pt 薄膜，以 CO 为探针分子，运用原位红外光谱研究薄膜的特殊红外性能，并获得粗糙度较大且具有显著红外增强效应的枝晶 Pt 薄膜，在该 Pt 薄膜电极上，运用原位红外光谱，检测乙醇和氨电氧化过程中产生低覆盖的中间体。主要结果如下：

1、碱性介质中乙二醇在Pd上电氧化主要生成CO_2(碳酸根)，乙醇酸，乙二醛，乙醛酸，草酸；在很高电位 (>0.4 V)，有甲酸根的生成。在低电位区，乙二醇会解离吸附，产生桥式吸附态的CO (CO_B)。在四个C2中间体中，草酸根很稳定，乙醇酸，乙二醛和乙醛酸可进一步发生氧化，但其反应选择性是不一样的，乙醇酸和乙二醛更易生成碳酸根，而乙醛酸生成草酸根。乙二醇电氧化的循环伏安峰电流随着乙二醇浓度增加而增大，峰电位正移，且反应选择性也随浓度而发生变化：2 mM EG，主要生成CO_3^{2-}；20 mM EG，主要生成CO_3^{2-}和$C_2O_4^{2-}$；高浓度（0.1 M和1 M EG），主要生成CO_2，乙醇酸和乙醛酸。

2、采用方波电位法成功制备出枝晶状结构的Pt薄膜。随着电沉积时间的增加，薄膜厚度、枝晶上纳米粒子团聚程度，以及电极粗糙度都逐渐增大。Pt薄膜电极上吸附态CO的红外谱峰形状随沉积时间的增加，发生如下变化：谱峰为向下 (0 min，即本体Pt)→左高右低的双极峰 (3 min)→向下增强红外吸收 (6 min)→左高右低的双极峰 (9 min)→向上异常红外 (12 min)→左低右高的双极峰 (15 min)→向下增强红外吸收 (18 min)。增强红外效应和异常红外效应可以通过两种类Fano双极峰相互转化，这表明纳米材料薄膜所呈现出的特殊红外性能与纳米材料的尺度和聚集状态等密切相关。

3、方波处理时间为6 min时，所得到的枝晶状Pt电极同时具有较大的粗糙度

(R_r = 14)和显著的红外增强效应 (增强因子为10)，吸附态CO的红外谱峰强度可达到ΔR/R=0.20，远大于本体Pt（0.006）和传统铂黑电极（0.046），运用该枝晶状Pt薄膜电极作为研究电极，可以用来检测电催化反应过程产生的一些低覆盖度的中间体。例如对于吸附态CO，可以检测到位于2450cm^{-1}的Pt-C键和C-O的非常微弱的组频峰；乙醇在Pt上电氧化主要产生CO_2和乙酸，吸附态物种除了观察到CO，还可以检测到吸附态的乙酸根，位于1400cm^{-1}。NH_3在Pt电氧化产生吸附态物种$NH_{2,ads}$，位于1240 cm^{-1}，并用$^{15}NH_3$同位素实验进行确认，该物种是产生N_2的活性中间体。

关键词：原位红外光谱；电催化；电氧化机理；枝晶状 Pt 薄膜；特殊红外性能；

Abstract

In this thesis, EG electrooxidation on a bulk Pd electrode in alkaline media was studied by cyclic voltammetry (CV) and *in situ* FTIR spectroscopy (*in situ* FTIRS). The emphasis was placed on the exploration of the mechanism of electrooxidation of EG and its C2 derivatives, as well as the effect of EG concentrations, through a quantitative spectral analytic method developed by our group's method. Besides, we successfully prepared dendritic Pt thin film on a bulk Pt by square wave potential. Using adsorbed CO as a molecular probe, we studied the anomalous infrared properties of these kinds of thin films, and obtained a dendritic Pt thin film electrode with significant IR enhancement. We further applied this dendritic Pt thin film to detect low-coverage intermediates produced from some electrocatalytic reactions (such as ethanol oxidation and ammonia oxidation). The main findings are as following:

1. In situ FTIR spectroscopic studies demonstrated that EG electrooxidation on Pd produces a series of solution species, such as glycolate, glyoxal, glyoxylate, oxalate, CO_2 (CO_3^{2-}), and formate in 0.1 M EG + 0.1 M NaOH. Besides solution species, adsorbed species, i.e., bridge-bonded CO (CO_B) can be observed. Some C2 species can be oxidized further, but the selectivity shows great difference. Glycolate and glyoxal show higher catalytic activity than glyoxylate, yielding more carbonate, while only glyoxylate can yield formate at the potential higher than 0.4 V. The reaction selectivity of EG oxidation also highly depends on its concentration. In the cyclic voltammograms recorded on the Pd electrode in 0.1 M NaOH, peak current of EG oxidation increases with increasing the concentration, and peak potential shifts positively. In situ FTIR results indicates that EG electrooxidation only yields CO_3^{2-} at the concentration of 2 mM EG; whereas $C_2O_4^{2-}$ and CO_3^{2-} are the main products during 20 mM EG electrooxidation. At higher concentration (0.1 M and 1 M), EG oxidation generates a majority of incomplete oxidized products (glycolate and

glyoxylate) and a small amount of CO_2.

2. Dendritic Pt thin films were electrodeposited on a bulk Pt electrode in 10 mM K_2PtCl_6 +0.3 mM $PbAc_2$ + 0.5 M $HClO_4$ by square wave potential. As deposition time increases, the length of Pt dendrites increases from about 400 nm to 900 nm, and the distribution density of Pt nanoparticles (~ 10 nm) consisting of Pt dendrites increases greatly, reducing the distance between nanoparticles. The IR shapes of adsorbed CO change as the following order: downward → bipolar (upward at high wavenumbers) → downward → bipolar (upward at high wavenumbers) → upward → bipolar (downward at high wavenumbers) → downward band with increasing deposition time. This result indicates that the anomalous infrared effects including Fano-like infrared effects (bipolar), surface enhanced IR absorption (SEIRA, enhanced normal downward band) and abnormal IR effects (AIREs, enhanced abnormal upward band) are highly depended on the architecture of surface nanostructures, and can be converted one into another.

3. The dendritic Pt electrode electrodeposited for 6 min had a large IR enhanced absorption for adsorbed species. In comparison with conventional Pt black electrode and smooth Pt electrode, this dendritic Pt nanostructure can yield a very intensive infrared signal ($\Delta R/R = 0.20$) for adsorbed CO due to both high enhanced effect ($\Delta_{IR} = 10$) and moderate roughness ($R_r = 14$). This fractal Pt structure may be used as highly sensitive infrared substrate to detect low-coverage adsorbed species. For CO adsorption system, the very weak combination bands of $\nu_{Pt\text{-}C} + \nu_{C\equiv O}$ at 2450 cm^{-1}, whose band intensity is just about 1/3000 that of $\nu_{C\equiv O}$, can be detected for the first time. Ethanol electro-oxidation on dendritic Pt nanostructure mostly yields CO_2, acetic acid and adsorbed CO. In addition, adsorbed CH_3COO^- can be observed at 1400 cm^{-1}. As for ammonia oxidation on Pt, the adsorbed species $NH_{2,\,ads}$ (1240 cm^{-1}) acting as an active intermediate for the production of N_2, was successfully detected